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Effect of type of mixing water and sand on the physico-mechanical properties of magnesia cement masonry units

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Abstract This study has been conducted to investigate the influences of sand addition and mixing waters with different ratios on the physico-mechanical properties of magnesium oxychloride cement (MOC) masonry units. Three mixtures (M, MI and MII) were prepared to make magnesium oxychloride cement from the sand dunes as a filler material with some different additives. The mixture (M) was prepared by seawater instead of tap water in the mixing process, other mixtures (MI & MII) used drinking water. The physico-mechanical properties were studied in means of determination of bulk density, water absorption and compressive strength of the hardened MOC specimens cured in air at the lab ambient conditions for 3, 7, and 28 days. It was recognized that the compressive strengths decreased with the increase of sand dunes content. The specimens of the all cured mixtures fulfilled superior properties compared with the required limits for concrete and limestone masonry units of a heavy density type. Also, it was found that using of the seawater leads to increase the physico-mechanical properties of the MOC specimens and can be used as mixing water in the manufacture of masonry units instead of the traditional drink water after ensuring of the other demanded governing properties.

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Introduction

Magnesium oxychloride cement, denoted as MOC, was first discovered and prepared by Sorel in 1867. It is commonly referred to as a Sorel cement, magnesia cement and magnesium oxychloride cement. The Sorel cement is a hydraulic cement mixture of magnesium oxide with magnesium chloride together with filler materials. It is one of the strongest cements and has many superior properties than Portland cement, such as high strength, negligible volume changes and quick setting

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times with high early strength. In addition, it does not require humid curing conditions [1]. MOC is formed by mixing powdered magnesium oxide with a concentrated solution of magnesium chloride. Magnesium oxide, or magnesia, is a white solid mineral that occurs naturally as periclase and is a source of magnesium. The majority of magnesium oxide produced today is obtained by processing of naturally occurring materials, such as magnesite (magnesium carbonate), magnesium chloride rich brine and seawater. Reactive magnesium oxide, or calcined magnesia, is normally obtained by calcination of magnesite (MgCO_3) at a temperature around 750°C . The quality or reactivity of the formed magnesium oxide powder is largely affected by its thermal history (calcination temperature and firing duration) and particle size. The reactivity of MgO increases by the decrease of particle size [2,3]. Generally, the lower the burning temperature of calcination (less than 750°C) and the finer grinding (95% passing $45\text{ }\mu\text{m}$), the generated magnesia will characterize by its highest reactivity (surface area more than $90\text{ m}^2/\text{g}$) and fastest hydration to attain its maximum strength after less than 3 days [4]. From a recent work [2], it was found that the most suitable molar ratios of MgO/MgCl_2 and $\text{H}_2\text{O}/\text{MgCl}_2$ existed between 11–17 and 12–18, respectively for possessing MOC paste rich in $5\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ phase.

The major commercial applications of magnesium oxychloride cement are in industrial flooring, fire protection, grinding wheels, rendering wall insulation panels and bunkers [5]. However, its outdoor application scope is greatly limited by resolution in water. The prolonged contact with water results in leaching of MgCl_2 from the bond phase $5\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ leaving brucite $\text{Mg}(\text{OH})_2$ as a binding phase, which leads to reduce strength of the body.

A lot of researchers have long been worked to improve the water-resistance of magnesium oxychloride, particularly at high temperatures [6–9]. Various additives have been added to overcome the problem of water solubility, with varying degrees of success. It was found that some additives can greatly improve the water resistance of MOC cements, such as phosphoric acid and soluble phosphates, including the phosphates of alkali metals, alkali earth metals, iron, aluminum, and ammonia. Even small amount of these compounds can improve the water resistance of MOC very much. It is interesting to mention here that the addition of soluble phosphates to MOC's improves water resistance by the formation of insoluble phosphate complexes which could influence the hydrolysis of Mg^{2+} ions in the solution [10]. In general, the addition of phosphoric acid more than the necessary ($>1\%$ of the MOC paste mass) causes the compressive strength of dry specimens cured for 15 days to be decreased [8].

The setting and hardening of the MOC takes place in a through-solution reaction [11]. The four main reaction phases in the ternary MOC system are $2\text{MgO}(\text{OH})_2\cdot\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ (phase 2), $3\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ (phase 3), $5\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ (phase 5), $9\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 5\text{H}_2\text{O}$ (phase 9) and $\text{Mg}(\text{OH})_2$. These phases are existed in the ternary system at different temperatures [12]. It is known that the hydrated phases (5 and 3) are the major reaction products responsible for hardening and strength of MOC and usually occur as well-crystallized needles [1].

A research study [13] conducted on magnesia-phosphate cement reinforced with fibers, recorded that the test cement

pastes develop after 3 hours mechanical properties comparable with ordinary Portland cement composites tested at 28 days. This work mainly aims to save drinking water as mixing water by conducting a comparative study between magnesia cement mixtures to illustrate the effect of the type of used water and sand addition on physico-mechanical properties of the hardened magnesium oxychloride cement pastes cured in air up to 28 days.

Experimental

Materials

Magnesite as a raw material was obtained from the quarries of magnesite deposits located at the southern Eastern Desert of Egypt. The calcination was done in a mazut kiln at a processing company in the industrial area at Helwan Governorate. The raw material was fired at about 750°C for about 24 h and left to cool down inside the furnace until the ambient temperature then ground to $90\text{ }\mu\text{m}$ sieve. A white to light yellow color of caustic magnesia powder (MgO) was obtained and used in this research. The magnesium chloride employed was hygroscopic hexahydrate ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) crystals with a purity of 98% provided from China. The used sand was collected by the co-authors from the sand dunes situated along Cairo–El Wahat desert road, Western Desert, Egypt. The used mixing waters were drinking and seawaters; the drink water was a traditional tap water, while the seawater was taken from the coast of Alexandria city (Egypt) at the Mediterranean Sea. Also, additives were used in the present study; E-glass fiber (25 mm length, density of 2.55 g/cm^3 , tensile strength of 2000 MPa and young modulus of 80 GPa) and powder salt of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). Additions of fibers and $\text{NH}_4\text{H}_2\text{PO}_4$ to these composites were used for improving the strength and water solubility of the magnesia cement pastes, respectively.

Sample preparation

The magnesium chloride hexahydrate and ammonium dihydrogen phosphate were first dissolved in water before mixing with magnesium oxide powder to form MOC paste. Subsequently, the sand and E-glass fibers were added consecutively to the mixture in the same bowl and then mixed with the mixing water mechanically to form homogeneous MOC pastes. The residual water demand as well as the sand was added to achieve good workability and desired concentration, respectively. Following mixing, the mixed pastes were poured into plastic cylindrical molds of 5 cm diameter and 10 cm length and vibrated manually. Care was considered to reduce the amount of air voids as much as possible. The hardened MOC specimens were demolded 5 h after casting, then cured in the ambient lab environment ($26 \pm 2^\circ\text{C}$ and relative humidity $40 \pm 5\%$) for 3, 7 and 28 days. The mixing procedures were the same for all pastes and 20 cylindrical specimens were made from each mixture. In order to conduct a comparative study between the MOC pastes of different ingredients ratios using variable mixing waters. Three suggested mixtures were prepared for studying the physico-mechanical properties of the air cured specimens at different ages. In an abbreviated notation, the studied mixtures were designated as M, MI and

Table 1 Mixture proportions of the prepared MOC pastes.

Mix code	Mixture composition, weight ratio						Type of mixing water
	MgO	MgCl ₂	Sand	Glass fiber, by wt., % of the cement mass	NH ₄ H ₂ PO ₄ by wt., % of the cement	W/S ratio	
M	1	0.5	1	0.4	0.7	9.42	Seawater
MI	1	0.5	1	0.4	0.7	10.09	Tap water
MII	1	0.5	2	0.4	0.7	10.41	Tap water

MII. Mixture (M) was mixed with seawater whereas the other mixtures (MI & MII) were mixed with tap water. The used material proportions with the type of mixing water for the various mixtures are given in Table 1.

Test methods

The chemical analysis was performed on the ground pressed magnesite and sand powders using Philips PW 1400 XRF as well as following the test method described in the American Society for Testing and Materials [14]. The chemical analysis of the mixing waters was carried out using classical analytical techniques including volumetric and gravimetric analysis described in water chemistry handbooks. The pH was measured at 20 °C by Jenway 3510(UK) digital pH meter with combined glass electrode following the test method reported [15].

The mineral composition of the used magnesite was characterized by X-ray diffraction (XRD). The XRD analysis was carried out on the powdered sample passed through 25 µm sieve using XRD apparatus of X'pert Pro type (Netherlands). The analysis was run using Cu Kα radiation in the range 2θ from 5°–50° with acceleration voltage conditions of 40 kV and 40 mA. The interpretation of the obtained minerals was attained by the X'Pert high score PDF-2 database software on CD-Release 2010. The physico-mechanical properties of the hardened magnesium oxychloride cement at curing times of 3, 7 and 28 days were assessed. The tested properties are bulk density, water absorption as well as compressive strength and determined according to ASTM's standards [16–18].

The particle size distribution of the used sand due sample was determined using dry sieve analysis method according to the Egyptian specification, ES, [19].

The strength retention coefficient is defined by the following formula:

$$SRC_n = CSD_n / CSw_n$$

where; SRC_n- Strength retention coefficient of the MOC hardened specimen at a specific time. CSD_n- Dry compressive strength of the MOC specimen at a specific air curing time. CSw_n- Wet compressive strength of the MOC specimen at a specific water soaking time. n- The specific testing time.

Results and discussion

Characterizations of the magnesite powder, mixing waters and sand dunes

The chemical composition of the calcined magnesite and sand is listed in Table 2. MgO as expected is the main oxide (81.74%). The high value of loss on ignition is mainly due to releasing of

Table 2 Chemical analysis of the magnesite and sand dunes used.

Constituent oxide%	Magnesite	Sand dunes
SiO ₂	1.20	93.88
Al ₂ O ₃	0.10	3.76
Fe ₂ O ₃	1.28	0.68
CaO	2.35	0.55
MgO	81.74	0.37
Na ₂ O	0.01	0.21
K ₂ O	0.01	0.09
SO ₃	0.43	0.02
TiO ₂	0.02	0.10
P ₂ O ₅	0.01	0.01
L.O.I	12.82	0.23

high content of CO₂ during ignition. The analyzed sand is mainly composed of SiO₂ (93.88%). Moreover, magnesite was characterized for mineral composition by using X-ray diffraction technique (XRD) as shown in Fig. 1. It is essentially composed of periclase mineral (MgO), and subsidiary of portlandite [Ca(OH)₂] and calcite (CaCO₃) minerals. The mineral composition of the analyzed magnesite is in consistency with its chemical composition. Table 3 also illustrates the chemical composition of the used mixing waters. Seawater contains more dissolved ions than those of fresh water. However, the ratios of various solutes differ dramatically. The chemical result of the seawater is within the average content of the Mediterranean Seawater. Moreover, the result of the tap water is agreed with the allowable limits for the chemical aspects of drinking water by the World Health Organization (WHO).

The particle size analysis of the sand sample is illustrated in Fig. 2. From the sieve analysis result, the studied sample is out of limits of the fine sized-sand particles; fine upper limit

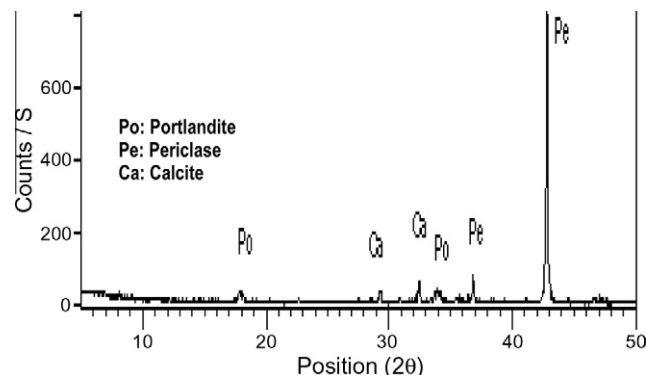
**Fig. 1** X-ray diffraction pattern of the MgO powder.

Table 3 Major ions composition, pH and total dissolved salts of the tap water and seawater used.

Ingredient	Tap water	Seawater
Chloride (Cl^-), ppm	200	19345
Sodium (Na^+), ppm	40	10752
Sulfate (SO_4^{2-}), ppm	300	2701
Magnesium (Mg^{2+}), ppm	12	1295
Calcium (Ca^{2+}), ppm	75	416
Potassium (K^+), ppm	3	390
pH	6.8	7.6
Total dissolved salts (T.D.S)	450	36544

(F.U.L.) and fine lower limit (F.L.L.). It needs slightly coarse particles to achieve the limits. The particle size analysis of the sand sample shows that the particles are slightly larger than 150 μm and less than 600 μm .

Physico-mechanical properties

Physical properties

The water/solid ratio (W/S), bulk density and water absorption of the MOC specimens of the three mixtures are listed in Table 4. The water/solid ratio of the M, MI and MII are 9.42, 10.09 and 10.41%, while their bulk densities are 2.50, 2.50 and 2.55 g/cm^3 , respectively. It is clear that the bulk density increases with the increase of both of sand content and water/solid ratio. This is due to the specific gravity of sand. The specimens of MII with the highest content of sand possess the highest bulk density.

The increase of sand with the simultaneous increasing of water/solid ratio leads to increase the bulk density of the cement pastes. Moreover, the soluble phosphate as $\text{NH}_4\text{H}_2\text{PO}_4$ reacts with magnesium hydroxide and produces difficult dissolving complicated hydrated products and gels, which can fill the capillary pores to give more compact body of MOC paste [8].

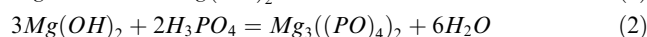
The water absorption of the hardened specimens of M, MI and MII cured in the lab ambient conditions for 28 days, and then immersed in tap water for 24 h is 2.30, 1.90 and 1.58%, respectively. This may be attributed to the presence of sand in appreciable amount, particularly in MII. It is very fine

Table 4 The water/solid ratio, bulk density and water absorption of the hardened M, MI and MII specimens.

Mix code	W/S ratio%	Bulk density g/cm^3	Water absorption%
M	9.42	2.50	2.30
MI	10.09	2.50	1.90
MI	10.41	2.55	1.58

and acts as water repellent filler material. The presence of phosphate group in $\text{NH}_4\text{H}_2\text{PO}_4$ reacts with $\text{Mg}(\text{OH})_2$ to produce magnesium oxyphosphate compound. This product is insoluble, protect all surfaces of the phase-5 grains in the pastes from the decomposition caused by water and fill its capillary pores with decreasing water absorption [1]. As the bulk density of the cement paste increases the total porosity as well as the water absorption decrease.

It is expected that the addition of soluble phosphates to MOCs will improve the water resistance of the hardened specimens by the precipitation of totally insoluble phosphate complexes [10], according to following equations:

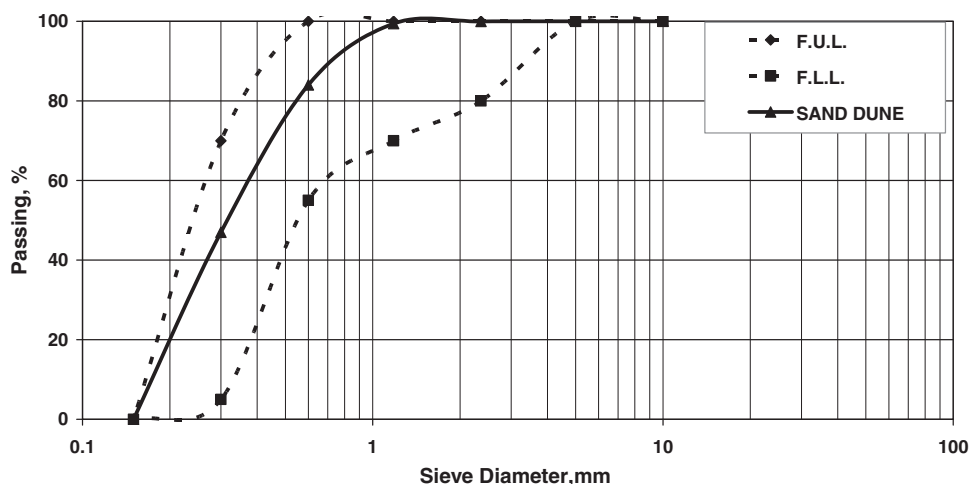


Mechanical properties

Dry compressive strength

The results of dry compressive strength of the M, MI and MII specimens cured for 3, 7 and 28 days at the lab ambient conditions are plotted in Fig. 3. It is observed that the hardened specimens of the mixture M (mixed by the seawater) give higher strength values than those of mixtures MI and MII (mixed by the tap water) at all curing times. For all specimen mixtures, the compressive strengths increase with the curing time increasing.

Also, using seawater instead of tap water leads to increase the compressive strength of the hardened specimen pastes. Moreover, as the sand content increases, the compressive strength decreases. This is due to the decrease of the cement

**Fig. 2** Grain size distribution (dry sieves analysis) of the sand dune sample.

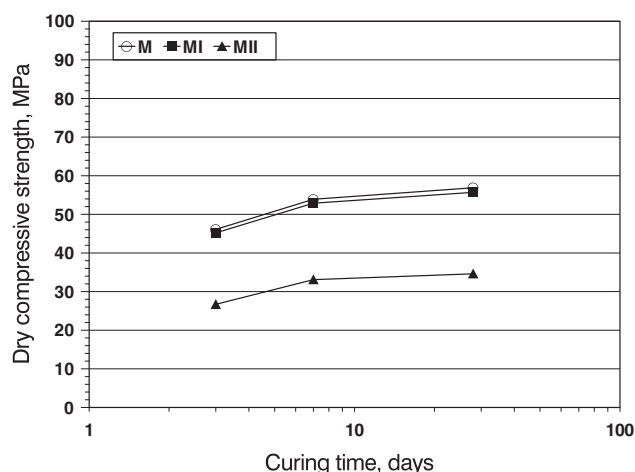


Fig. 3 Dry compressive strength of the hardened cement specimens of different mixtures with curing times up to 28 days.

part and the increase of sand which has no hydration characteristics and acts as water repellent material.

In industrial applications, seawater is the primary commercial source of magnesium oxide. The water is first evaporated, leaving a solid material that's very high in table salt (NaCl) and magnesium compounds such as magnesium chloride ($MgCl_2$). The seawater is treated with hydrated lime to produce calcium chloride and precipitate magnesium hydroxide. Accordingly, Mg^{2+} ions in the seawater (as additional source) increase the $Mg(OH)_2$ content and the hydrated phases as well, mostly by their penetration in the pastes. The formed hydrated phases, 5 or 3 are closely related to the stable polynuclear complexes $[Mg_x(OH)_y(H_2O)_z]^{2-y}$ produced by the hydrolysis of Mg^{2+} ions [1]. This may interpret results of the hardened specimens prepared by mixing the Mediterranean seawater (M); it has the highest compressive strength values.

Wet compressive strength

Results of wet compressive strength of the hardened M, MI and MII specimens of air cured for 3, 7 and 28 days at the

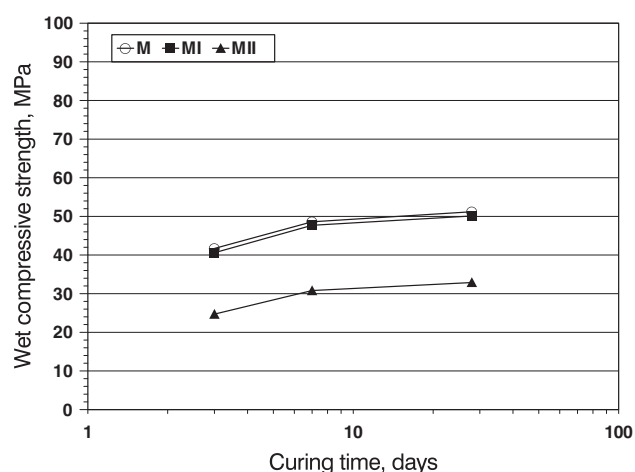


Fig. 4 Wet compressive strength of hardened cement specimens of different mixtures during progressing the curing times up to 28 days.

Table 5 The strength retention coefficients (SRC_n) of the MOC specimens of the different mixtures cured for 3, 7 and 28 days.

Mix code	SRC_3	SRC_7	SRC_{28}
M	0.95	0.97	0.97
MI	0.96	0.96	0.96
II	0.92	0.93	0.95

ambient lab conditions are depicted in Fig. 4. The results indicate that the specimens are slightly lower than these of the dry and follow their corresponding trend and arrangement. Specimens of M give higher values of wet compressive strength than MI and MII at all curing times. These results explain that using seawater increase the compressive strength. This may be due to its lower content of sand than those mixed with drink water, in addition to the precipitation of NaCl in pores. Also, it can be seen that the high content of sand (2 parts) does not improve either dry or wet compressive strengths and is not desirable due to its negative effect as recognized on the properties of the specimens of MII. These results are in agreement with a previous scientific research [20].

From the results of both dry and wet compressive strength of the hardened M, MI and MII specimens, the strength retention coefficients was calculated as shown in Table 5. The highest value is achieved by specimens M and the lowest one for those of MII at all curing times. This is in concordant with achievable results of the dry and wet compressive strength of the specimens of the studied mixtures. It is worthy to note here that the phosphate group in $NH_4H_2PO_4$ reacts with $Mg(OH)_2$ and produces difficult dissolving complicated hydrated products and gels, which can fill the pore capillaries with decreasing the contact probability between inner structure substances and exterior water. So, it is expected to improve the water-resistance of the brick masonry units. The presence of $NH_4H_2PO_4$ improves the wet compressive strength and consequently, increases the strength retention coefficient. Thus, when the hardened MOC pastes made from a small quantity of the soluble phosphates are immersed in water, the (phase- 5) or (phase- 3) will not be decomposed by water. Therefore, the strength of the hardened MOC pastes remains unchanged in water [1].

The results of the physico-mechanical properties for the MOC specimens of all mixtures are more than these recommended for concrete and limestone masonry units (Heavy density type) according to the Egyptian Code, ECCS, [21]. In addition, these results secure more than the average value of the ordinary Portland cement concrete pastes cured for 28 days.

Conclusions

Based on the experimental data obtained from the preliminary investigations, the following conclusions can be drawn.

1. The specimens of mixture M, mixed by the seawater, have the superior physico-mechanical properties at all curing times followed by those of mixtures MI then MII.

2. The bulk density increase and both of the compressive strength and water absorption decrease with the sand content.
3. The seawater can be used instead of tap water in the studied mixtures for making masonry units to save drinking water for useful purposes.

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